

DERWENT-ACC-NO: 2002-017885

DERWENT-WEEK: 200203

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TITLE: Metal modified small-porosity P-Si-Al molecular sieve  
catalyst, its preparing process and its use

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PRIORITY-DATA: 1996CN-0115362 (June 7, 1996)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
CN 1167654 A	December 17, 1997	N/A	000	B01J 029/85

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
CN 1167654A	N/A	1996CN-0115362	June 7, 1996

INT-CL (IPC): B01J029/85, C07C011/04 , C07C011/06

ABSTRACTED-PUB-NO: CN 1167654A

BASIC-ABSTRACT:

NOVELTY - A metal modified SAPO-34 type of molecular sieve catalyst can be used in conversion of methanol or dimethyl ether to lower olefin. The modifying metal may be Cu, Co, Ni, Ca, Ba, or Sr and the adhesive and pore-forming agent are used in conjunction with the modifying metal. The modifying metal ions are introduced by impregnation when or after the molecular sieve is synthesized. The catalyst features higher activity (about 100% of conversion), high selectivity of product (especially ethylene) and reuse after regeneration.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: METAL MODIFIED POROUS P AL MOLECULAR SIEVE CATALYST PREPARATION  
PROCESS

DERWENT-CLASS: A41 E17 H04 J04

CPI-CODES: A01-D13; E10-J02C3; H04-E; H04-F02E; J04-E04; N06-A; N06-B03;

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C2002-005251

PTO 03-3718

Chinese Article

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Metal Modified Small Aperture Ph-Si-Al Molecular Sieve Catalyst  
and Its Preparation and Applications

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Washington, D.C.

June 2003

Translated by: Schreiber Translations, Inc.

Country : People's Republic of China

Document No. : N/A

Document Type : Patent Application

Language : Chinese

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IPC : B01J 29/85

Application Date : June 7, 1996

Publication Date : December 17, 1997

Foreign Language Title : Jinshu Gaixing Xiaokong Lin-Gui-Lu  
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English Title : Metal Modified Small Aperture Ph-Si-  
Al Molecular Sieve Catalyst and Its  
Preparation and Applications

[57] Abstract

This invention concerns a kind of metal modified SAPO-34 molecular sieve catalyst used in the inversion of methyl alcohol or dimethyle ether into low-carbon olefin. The modifying metal element includes Cu, Co, Ni, Ca, Ba, or Sr. Binders and aperture medium are added in the amount of 30-80% and 1-15% of catalyst weight respectively. In the catalyst, the modifying metal ions are introduced with immersion technique during or after the synthesis of molecular sieve. The catalyst has high activity (the rate of inversion is close to 100%) when it is used in the reaction of methyl alcohol or dimethyle ether into low-carbon olefin. The product of low-carbon olefin, especially ethylene has high selectivity. The catalyst can be reused repeatedly.

## Claims

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1. This invention involves a kind of metal modified SAPO-34 molecular sieve catalyst used in the inversion of methyl alcohol or dimethyle ether into low-carbon olefin, wherein the modifying metal element is Cu, Co, Ni, Ca, Ba, or Sr. The content of metal element is 0.01~0.15% of the weight of molecular sieve.

2. According to the catalyst as described in Item 1 of the Claims, binders and aperture medium are added in the amount of 30~80% and 1~15% of catalyst weight respectively. The binder is one or two kinds of mixtures of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  or  $\text{MgO}$ . The aperture medium is sesbania powder, methyl carboxyl cellulose, or starch.

3. According to the catalyst as described in Items 1 and 2, the modifying metal element is Ca, the binder is  $\text{SiO}_2$ , and the aperture medium is sesbania powder.

4. This invention involves the preparation method of catalyst as described in Item 1 of the Claims, wherein the preparation procedure is as follows:

1) Apply conventional techniques to synthesize SAPO-34 molecular sieve or directly select commercial SAPO-34 molecular sieve as the subject sieve;

2) Introduce modifying metal ions.

a. In the synthesized SAPO-34 molecular sieve, add simultaneously soluble saline solution containing metal ions, such as nitrate solution so as to introduce metal cations into the molecular sieve;

b. Apply immersion technique by using soluble saline solutions containing metal cations, such as nitrate solution to immerse SAPO-34 molecular sieve;

3) Catalyst preparation

Use the materials as described in Item 2 to add specified amount of binders and aperture medium. The product catalyst is prepared after going through the processes of drying at 50~120°C and baking at 350~650°C for 1~8 hours.

## Instructions

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Metal Modified Small Aperture Ph-Si-Al Molecular Sieve Catalyst  
and Its Preparation and Applications

This invention concerns a kind of high selectivity, metal modified small aperture SAPO-34 molecular sieve catalyst with dimethyle ether or methyl alcohol as the raw material for use in preparing low-carbon olefins such as ethylene and propylene, the preparation method, and the application of this kind of catalyst in synthesizing low-carbon olefins such as ethylene and propylene.

Ethylene and propylene are two kinds of basic raw materials with the largest masses and multiple application purposes in petrochemical industry. They are acclaimed as mother of modern organize synthesis industry. Many industrial developed nations in the world have been competing in the development of production techniques in this aspect. Until today, however, ethylene and propylene are still mainly produced through the traditional industrial production method of light oil splitting decomposition from crude oil raw materials. The impact of two oil crises in 1970s promoted what was called C<sub>1</sub> chemical research

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<sup>1</sup> Numbers in the margin indicate pagination in the foreign text.

and development focusing on preparation of pulp carbon olefin or gasoline fuel from non-crude oil raw materials, and started an upsurge worldwide on the research in  $C_1$  chemistry. The most representative research achievements in this aspect was two new manufacturing techniques of low-carbon olefins (MTO) and gasoline (MTG) with methyl alcohol as the raw material and ZSM-5 zeolite as the catalyst made by the U.S. Mobile Corporation in mid 1970s. After that, attempts have been made in using erionite, rhodopotassium zeolite, silk zeolite, ZSM-34, or ZSM-45 as MTO process catalyst. In mid 1980s, the U.S. United Carbon Compound (U.C.C.) developed small aperture Ph-Si-Al SAPO-34 molecular sieve as a new generation catalyst used in the MTO anodization of active substrate. This catalyst is advantageous in that its ethylene selectivity is twice as high as that of medium-size aperture ZSM-5 catalyst and reaches 50-60%. In early 1990s, the applicant of this invention once presented a new reaction technical process (called SDTO) of making low-carbon olefins from dimethyle ether, as seen in the document of Chinese Patent Publication No. CN1067878A. Afterwards, the applicant presented a series of SAPO-34 molecular sieve catalyst preparation methods used in the new technical process, as well as the technique for transformation of methyl alcohol or dimethyle ether into low-carbon olefins, which are documented in



the Chinese Patent Publication No. CN1087292A, CN1096496A, and CN1106715A. The raw materials used in the SAPO-34 molecular sieve preparation method under the above-mentioned techniques are resourceful and cost-effective. The catalyst offers very high conversion rate and high low-carbon olefin selectivity in methyl alcohol and dimethyle ether transformation reactions, and therefore can be used in industrial production. Compared to medium-size aperture ZSM-5 zeolite, the small aperture SAPO-34 molecular sieve has higher selectivity to low-carbon olefins in the MTO process. However, its surface acidity is still inappropriate and has to be revised in order to further enhance the selectivity to low-carbon olefins, especially the selectivity to ethylene.

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The purpose of this invention is to provide a small aperture SAPO-34 molecular sieve catalyst having high catalytic activity to the transformation reaction of methyl alcohol and/or dimethyle ether into low-carbon olefins and having high selectivity to reaction product, especially to ethylene.

To achieve the invention objective, the inventor made further research based on early studies and proposed an improved scheme. First, different metal ions such as two-valence Cu, Co or Ni ions and especially Ca, Ba, or Sr alkaline-earth ions are

introduced in the synthesizing process. The content of metal ions is 0.01~0.15%, and 0.05~0.1% at best, of the weight of molecular sieve. The introduction of these metal cations can help adjust surface enzymes and change the size of aperture of SAPO-34 molecular sieve in order to improve ethylene selectivity. The modification of SAPO-34 molecules can be conducted after the molecules are synthesized. The above-mentioned metal ions can be introduced through ion exchange or metal-salt immersion. Besides, the water heat treatment in 700~800°C conditions can be applied for further adjustment. The above modification approach can help adjust acidity, modify aperture size, and stabilize the framework of SAPO-34 molecular sieve.

Secondly, zeolite molecular sieve has poor self-binding property. As such, it is essential to add certain amount of binders in order to improve the mechanical intensity of catalyst. The proper binders meeting the practical requirements shall be weak acidity or alkaline materials, and are best neutral oxidate materials such as  $\text{SiP}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{CaO}$  and their mixtures. The addition accounts for 30~80% weight of the molecular sieve. At the same time, certain amount of organic aperture medium shall be added for the purpose of undertaking secondary catalyst aperture determination. The materials that

can be used as aperture medium mainly include methyl carboxyl cellulose, starch, and sesbania powder. The consumption of aperture medium is 1~15% catalyst weight. Specifically, the catalyst preparation procedure is as follows:

1. Synthesize of SAPO-34 molecular sieves. This can be done with conventional techniques or commercial SAPO-34 molecular sieves.

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2. Introduce metal ions.

- a. In the synthesized SAPO-34 molecular sieve, add simultaneously soluble saline solution containing metal ions, such as nitrate solution so as to introduce metal cations into the molecular sieve;

- b. Apply immersion technique by using soluble saline solutions containing metal cations, such as nitrate solution to immerse SAPO-34 molecular sieve;

3. Prepare catalyst.

Use the materials as described in Item 2 of the Claims to add specified amount of binders and aperture medium. The product catalyst is prepared after going through the processes of drying at 50~120°C and baking at 350~650°C for 1~8 hours.

The above catalyst is used in the transformation reaction of methyl alcohol and/or dimethyle ether into low-carbon olefins

with the following reaction conditions: The reaction temperature is 500~600°C. The optimum temperature is 530~570°C. The reaction pressure is constant pressure. The most appropriate pressure is 0.01~10.05MPa. The reactant feeding speed in vacancy is 1~100h<sup>-1</sup>. The optimum speed is 4~10h<sup>-1</sup>. Upon losing its activity, the catalyst can be burnt to regenerate in the following conditions: The regeneration temperature is 550~650°C. The optimum temperature is 590~610°C. The regeneration time is 5~30 minutes. The best regeneration time is 8~12 minutes. The catalyst can be burnt in the air, nitrogen and air, or the air containing saturated vapors. The techniques employed in the invention are further explained through the following implementations.

Implementation example 1: Preparation of SAPO-34 molecular sieve

Add the solution containing 86.4g normal phosphate and 165g de-ionized water into the solution containing 109.8g zeolite (the water content is 31.7%) and 100g de-ionized water, and the solution containing 333.5g silicon colloidal sols (the SiO<sub>2</sub> content is 26.45%), 58.8g NaOH, and 21.1g de-ionized water. The mixture solution is well mixed and then added with 78.0g triethylamine and 21.1g de-ionized water. Stir the mixture for 3 hours until it is evenly mixed. Load the mixture into a stainless stilllage. Apply ageing at room temperature for 48

hours and then apply crystallizing process at 200°C for 50 hours. The product is filtered, cleansed, and dried (at 120°C for 24 hours). The X-ray powder diffraction confirms that the product is pure SAPO-34 molecular sieve.

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Implementation example 2: Preparation of modifier-included SAPO-34 molecular sieve

Bake SAPO-34 molecular powder obtained in implementation example 1 for 2 hours at 350°C, 2 hours at 450°C, and 3 hours at 550°C. Take 25g original baked powder and place in 250ml, 10% concentration calcium nitrate water solution. Stir the solution at 80°C and filter out unnecessary solution. Bake for 24 hours at 110°C and 4 hours at 550°C to obtain Ca-contained SAPO-34 molecular sieve ( $\text{Ca}^{++}$  content is 0.05%wt in finished product). At this point, the intensity of surface acid of the molecular sieve is weaker than that of the prototype molecular sieve (TPD de-ammonia method shows that the acidity of modified catalyst is about 50% that of prototype SAPO-34 molecular sieve catalyst). Moreover, the thermal stability of the molecular sieve is improved. The destructive peak temperature of the molecular sieve framework is enhanced from 1060~1100°C in the prototype sieve to over 1200°C in the modified sieve.

Implementation example 3: Preparation of catalyst

Take 25g molecular sieve obtained from implementation example 2. Add 94.4g silicon colloidal sols (the SiO<sub>2</sub> content is 26.5%wt) and 2g sesbania powder. Fully and evenly stir the materials and then undertake spraying and forming operation on spraying and drying equipment at 150°C to make microspheric finished catalyst C with the average particle variation of 40~60µm. The pile-equivalent weight of the catalyst is 0.62g/cm<sup>3</sup>. The wear-away loss of the catalyst under 2000h cold impact at room temperature is less than 20%wt. Repeat the above method but without adding sesbania powder to make catalyst D. The catalyst aperture structure is listed in Table 1.

Table 1 Effect of Aperture Medium on Aperture Structure

Sample	Aperture Medium Amount wt%	BETU Surface M <sup>2</sup> /g	Aperture Volume	Micro- aperture Volume ml/g	Average Aperture Diameter A°
C	8	267.52	0.2223	0.0908	25.06
D	0	175.07	0.3326	0.0278	54.64

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#### Implementation example 5: Catalyst property

In the transformation reaction of methyl alcohol into low-carbon olefins, employ fixed-bed catalyst reaction apparatus.

The reactor is a silicon glass tube. The charge amount of catalyst is 1.28g. Before the reaction starts, increase the catalyst temperature in 60ml nitrogen flow to 550°C and activate for 1 hour. The reaction raw material is carried into the reactor by nitrogen. In the reaction raw material, the mole content of methyl alcohol is 35%. The weight speed in vacancy WHSV of methyl alcohol is  $2h^{-1}$ . The reaction pressure is 0.05MPa. The reaction is undergone for 1 hour under 400°C condition. The sieves A, B prepared in implementation examples 1 and 2 are used as catalyst. The reaction results are shown in Table 2.

Table 2

Catalyst	Methyl Alcohol Conversion Rate (%)	$C_2^=$ Selectivity (%)	$C_3^= \sim C_4^=$ Selectivity (%)
A	100	40.77	45.33
B	100	49.03	41.53

#### Implementation example 5: Catalyst property 2

The fluidized bed reaction apparatus is used. The fluidized reactor is made of silicon glass. Treat SAPO-34 molecular sieve catalyst C provided in implementation example 3 for 24 hours at 600°C to obtain finished catalyst E. Fill 15ml (about 10g) catalyst E in the fluidized reactor and pump into methyl alcohol

or dimethyle ether as reaction raw materials. Before the formal reaction test is started, use pure nitrogen to conduct activation treatment to catalyst E1 for 1 hour at 550°C, and then switch in reaction of transformation of methyl alcohol or dimethyle ether into low-carbon olefins. The results of reaction after 10 minutes in the conditions of 550°C reaction temperature and 6.45h<sup>-1</sup> weight speed in vacancy of methyl alcohol (or 7.16h<sup>-1</sup> weight speed in vacancy of dimethyle ether) are listed in Table 3.

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Table 3

Reaction Raw Material	Olefin Product Composition %wt			
	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> <sup>+</sup> ~ C <sub>4</sub> <sup>+</sup>
Methyl Alcohol	6.33	62.79	22.34	89.57
Dimethyle Ether	6.42	59.35	24.22	88.32

#### Implementation example 6: Catalyst property 3

Apply exactly the same fluidized reaction apparatus and catalyst E as the above implementation example 5. Use methyl alcohol as the reaction raw material. Change the reaction temperature and methyl alcohol feeding weight speed in vacancy and then conduct reaction for 10 minutes. The reaction results



are listed in Table 4. In all reaction conditions, the conversion rate of methyl alcohol is 100%.

Table 4

Reaction Conditions		Olefin Product Composition %wt			
Temperature °C	Methyl Alcohol Weight Speed in Vacancy h <sup>-1</sup>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> <sup>=</sup> - C <sub>4</sub> <sup>=</sup>
450	5.0	2.0	31.0	38.2	78.4
490	5.0	3.0	35.4	36.3	83.2
530	5.0	4.4	45.6	30.5	87.8
550	5.0	6.3	52.4	23.4	89.0
570	5.0	9.8	60.3	22.1	87.3
550	3.0	6.5	51.2	28.5	88.3
550	6.0	6.2	58.1	23.2	89.5
550	10.0	6.0	62.3	20.0	90.2

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It can be seen that the proper reaction temperature range is 530~550°C, while the proper weight speed in vacant for methyl alcohol is 5.0~10.0h<sup>-1</sup>.

Implementation example 7: Catalyst regeneration test

Apply exactly the same fluidized reaction apparatus and catalyst E as the above implementation example 5. Use dimethyle

ether as the reaction raw material. Conduct repeated reaction and catalyst regeneration test to catalyst E. The regeneration test results show that in 550-650°C temperature range, catalyst decoking can be done directly through burning in the air. If the applied regeneration temperature is lower, the coking time is longer, and vice versa. In all of the tests, coke can be removed in its entirety to restore the catalyst activity. For example, to remove coke at 550°C, the regeneration can be done in 30-40 minutes. If the burning temperature is 650°C, then the regeneration can be done in 5 minutes. The proper coke burning temperature is 600°C. The test results after reaction for 10 minutes in the air are shown in Table 5.

Table 5 Results of 100 Times Regeneration Test

Regeneration Times	0	10	30	60	80	100
Reaction Temperature °C	550	530	530	530	530	530
Olefin Selectivity % wt						
C <sub>2</sub> <sup>=</sup> Selectivity (%)	35.66	49.49	52.55	52.53	52.33	50.69
C <sub>3</sub> <sup>=</sup> Selectivity (%)	30.76	34.09	34.45	31.45	32.08	35.88
C <sub>3</sub> <sup>=</sup> - C <sub>4</sub> <sup>=</sup> Selectivity (%)	87.16	92.19	94.81	92.51	92.66	93.46

Reaction conditions: The weight speed in vacancy for dimethyle ether is 2.0h<sup>-1</sup>.

The conversion rate of dimethyle ether is ~100%.

[19]中华人民共和国专利局



[12] 发明专利申请公开说明书

[51]Int.Cl<sup>6</sup>

B01J 29/85

C07C 11/04 C07C 11/06

[21] 申请号 96115362.8

[43]公开日 1997年12月17日

[11] 公开号 CN 1167654A

[22]申请日 96.6.7

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PTO 2003-3718

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权利要求书 1 页 说明书 7 页 附图页数 0 页

[54]发明名称 金属改性小孔磷硅铝型分子筛催化剂及其制备方法和应用

[57]摘要

一种甲醇或二甲醚转化为低碳烯烃用金属改性SAPO-34型分子筛催化剂, 改性金属元素为Cu、Co、Ni、Ca、Ba或Sr, 并加入粘结剂和造孔剂, 其加入量分别为催化剂重的30~80%和1~15%。该催化剂是在分子筛的合成中或合成后用浸渍技术引入改性金属离子。该催化剂用于甲醇或二甲醚转化为低碳烯烃反应具有较高的活性(转化率接近100%), 产物低碳烯烃, 特别是乙烯的选择性高, 催化剂可反复再生使用。

(BJ)第1456号

## 权 利 要 求 书

1. 一种甲醇或二甲醚转化为低碳烯烃用金属改性 SAPO-34 型分子筛催化剂, 其特征在于改性金属元素 Cu、Co、Ni、Ca、Ba 或 Sr, 金属元素的含量为分子筛重量的 0.01~0.15%。

2. 按照权利要求 1 所述的催化剂, 其特征在于加入粘结剂和造孔剂, 其加入量分别为催化剂重的 30~80% 和 1~15%; 所谓粘结剂为  $\text{SiO}_2$ 、 $\text{Al}_2\text{O}_3$  或  $\text{MgO}$  中的一种或两种混合物; 所谓造孔剂为田菁粉, 羧甲基纤维素或淀粉。

3. 按照权利要求 1、2 所述的催化剂, 其特征在于改性金属元素为 Ca, 所用粘结剂为  $\text{SiO}_2$ , 所用造孔剂为田菁粉。

4. 一种按照权利要求 1 所述催化剂的制备方法, 其特征是按下步骤:

1) 按常规技术合成 SAPO-34 型分子筛或直接取商品 SAPO-34 型分子筛作物料;

2) 引入改性金属离子

a. 在合成 SAPO-34 分子筛中, 同时加入含金属离子的可溶性盐溶液, 如硝酸盐, 使金属阳离子引入分子筛中;

b. 利用浸渍技术, 用含金属离子的可溶性盐溶液, 如硝酸盐浸渍 SAPO-34 分子筛;

① 催化剂的制备

利用 2 的物料, 添加一定量的粘结剂和改孔剂后成型经干燥和焙烧后制得产品催化剂, 干燥于 50~120℃ 下进行, 焙烧于 350~650℃ 下进行 1~8 小时。

# 说明书

## 金属改性小孔磷硅铝型分子筛催化剂 及其制备方法和应用

本发明涉及一种由二甲醚或甲醇为原料高选择性制合成乙烯、丙烯等低碳烯烃反应的改性小孔 SAPO-34 型分子筛催化剂,其制备方法及以这种催化剂用于乙烯、丙烯等低碳烯烃的合成。

乙、丙烯是石化工业两种质量最大和用途很多的基础原料,被誉为现代有机合成工业之母,世界许多工业发达国家都在竞相发展这方面的生产技术,但至今获取它们的仍主要是传统原油原料的轻油裂解工业生产方法。七十年代两次石油危机的冲击,推进了非石油原料路线制取低碳烯烃或汽油燃料称为 C<sub>1</sub> 化学的开发研究工作,并且在当时形成了国际 C<sub>1</sub> 化学研究热潮。在这方面工作中最具代表性的是美国 Mobil 公司在七十年代中期由甲醇为原料及以 ZSM-5 沸石为催化剂的分别制取低碳烯烃 (MTO) 和汽油 (MTG) 的两种新工艺过程,随后又出现了以毛沸石,菱钾沸石,丝光沸石, ZSM-34 或 ZSM-45 作为 MTO 过程催化剂的尝试;在八十年代中期美国联合碳化物公司 (U. C. C) 开发出小孔磷硅铝 SAPO-34 分子筛为活性基质阳 MTO 过程新一代催化剂,该催化剂性能特点在于其乙烯选择性可比中孔 ZSM-5 催化剂时提高一倍,达 50~60%。本申请人曾于在九十年代初提出了一种由合成气烃由二甲醚制取低碳烯烃的新反应工艺 (称 SDTO) 过程,中国专利公开号 CN1067878A。随后又提出了一系列该新工艺所用 SAPO-34 分子筛催化剂的制取方法及用于甲醇或二甲醚转化为低碳烯烃反应的技术。中国专利公开号

CN1087292A, CN1096496A和CN1106715A。上述技术所提供的制备SAPO-34分子筛的方法所用原料来源丰富,价格低廉,催化剂对甲醇和二甲醚转化反应具有很高的转化率和低碳烯烃的选择性,可用于工业生产。但和中孔ZSM-5沸石相比,小孔SAPO-34分子筛用于MTO过程时虽然已有较高的对低碳烯烃的选择性,因其表面酸性仍不十分合适,还进行改质调整,来进一步提高对低碳烯烃,特别是对乙烯的选择性。

本发明的目的是提供一种对甲醇或/和二甲醚转化成低碳烯烃反应有高催化活性和对产物有高选择性,特别是对乙烯有很高选择性的小孔SAPO-34分子筛催化剂。

为实现本发明的目的,本发明者在前期工作的基础上进一步锐意研究,提出一处改进方案,首先通过合成过程中引入不同的金属离子,诸如两价阳离子Cu, Co或Ni,特别是碱土金属离子Ca, Ba或Sr金属的离子,金属离子的含量为分子筛重的0.01~0.15%,最好在0.05~0.1%。这些金属阳离子的引入,不仅可以调节表面酸性,也可改变SAPO-34分子筛的孔口大小,来达到改善乙烯选择性的目的。对于SAPO-34分子的改质处理,也可在其合成之后进行,可以通过离子交换或金属盐浸渍方式将上述金属离子引入。此外还可将用700~800℃条件下水热处理手段进一步调整。通过以上改质办法,不仅可以调整酸性,修饰孔口大小,也可稳定SAPO-34分子筛骨架作用。

其次,沸石分子筛由于其自身粘结性能差,必须加入一定的粘结剂,提高催化剂的机械强度,达到实用要求,合适的粘结剂应是弱酸,碱性,最好是中性氧化物材料,如 $\text{SiP}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{CaO}$ 以及它们的混合物等。它们的添加量为分子筛重的30~80%wt。此外,还应同时加入一定的有机物造孔剂,以达到对催化剂进行二次选孔的目的,可以用作造孔剂的主要有

羧甲基纤维素, 淀粉以及田菁粉材料, 造孔剂的用量为催化剂的1~15%wt。具体地说, 本发明催化剂的制备过程为: 1. 合成SAPO-34分子筛: 其方法可按常规技术进行, 也可利用商品SAPO-34分子筛。

## 2. 引入金属离子:

a. 在合成SAPO-34分子筛中, 同时加入含金属离子的可溶性盐溶液, 如硝酸盐, 使金属阳离子引入分子筛中;

b. 利用浸渍技术, 用含金属离子的可溶性盐溶液, 如硝酸盐浸渍SAPO-34分子筛;

## 3. 催化剂的制备

利用2的物料, 添加一定量的粘结剂和改孔剂后成型经干燥和焙烧后制得产品催化剂, 干燥于50~120℃下进行, 焙烧于350~650℃下进行1~8小时。

上述催化剂用于甲醇或/和二甲醚转化为低碳烯烃反应, 其反应条件为: 反应温度为: 500~600℃, 最佳温度为530~570℃, 反应压力为常压, 最适压力为0.01~10.05MPa, 反应物进料重料空速为1~100h<sup>-1</sup>, 最佳为4~10h<sup>-1</sup>。催化剂失活后可进行烧焦再生, 其条件为: 再生温度550~650℃, 最佳为590~610℃, 再生时间5~30分钟, 最佳为8~12分, 可用空气, 氮气与空气或含饱和水蒸汽的空气进行。下面通过实施例对本发明的技术给予进一步地说明。

### 实施例1 SAPO-34分子筛的制备

将86.4克正磷酸和165克去离子水的溶液, 依次与109.8克假勃姆石(含水量31.7%)及100克去离子水的溶液, 以及与333.5克硅溶胶(含SiO<sub>2</sub>26.45%wt) 58.8克NaOH及21.1克去离子水的溶液混合均匀后, 再往上述混合物中加入78.0克三乙胺与21.1克去离子水, 搅拌3小时至均匀, 装入不锈钢合成釜中。

在室温下老化48小时, 再在200℃下晶化50小时。产品经过滤, 洗涤和烘干(120℃, 24小时)。x-射线粉末衍射证该产物为纯净的SAPO-34分子筛。

### 实施例2 引入改质剂的SAPO-34分子筛的制备

由实施例1中得到的SAPO-34分子筛原粉, 经350℃2小时, 450℃2小时, 550℃3小时焙烧后, 取25克, 置于250ml浓度为10%的硝酸钙水溶液中, 在80℃条件下搅拌小时, 滤去多余溶液, 110℃烘干24小时以及550℃焙烧4小时, 即得含钙的SAPO-34分子筛。(成品中含Ca<sup>++</sup>量为0.05%wt) 此时的分子筛的表面酸强变已比原型有新减弱(TPD脱氨法表明, 改质后催化剂的酸量为原型SAPO-34分子筛催化剂的50%左右)。并且热稳定性已有加强, 分子筛骨架破坏峰温由原型的1060~1100℃升至改质后的1200℃以上。

### 实施例3 催化剂的制备

取实例2制得的分子筛25克往其中加入硅溶胶(其中SiO<sub>2</sub>含量26.5%wt) 94.4克, 同时又加入2克田菁粉, 将物料充分搅拌均匀, 再在喷雾干燥设备上和150℃条件下进行喷雾成型操作, 制得平均粒变为40~60μm的微球型成催化剂C, 该催化剂的堆化重为0.62g/cm<sup>3</sup>, 在室温下连续2000小时冷态冲击磨损失率<20%wt。重复上述方法, 但不加田菁粉制备出催化剂D。其孔结构列于下表1。

表1 造孔剂对孔结构的影响

样 品	造孔剂加入量 wt%	BETU表面 m <sup>2</sup> /g	孔容 ml/g	微孔体积 ml/g	平均孔径 Å°
C	8	267.52	0.2223	0.0908	25.06
D	0	175.07	0.3326	0.0278	54.64



#### 实施例4 催化剂的性能

甲醇转化为低碳烯烃反应, 采用固定床催化反应装置, 反应器为石英玻璃管, 催化剂装填量为1.28克, 反应前催化剂在60ml的氮气流中升温至550℃活化1小时, 反应原料由氮气携带进入反应器, 反应原料气中甲醇摩尔含量为35%, 甲醇重量空速 $\text{WHSV} 2 \text{ h}^{-1}$ , 反应压力为0.05MPa, 反应温度为400℃条件下反应1小时, 分别使用实例1, 2制备的分餐筛A、B为催化剂, 其反应结果列于表2。

表2

催化剂	甲醇转化率 (%)	$\text{C}_2$ 选择性 (%)	$\text{C}_3 \sim \text{C}_4$ 选择性 (%)
A	100	40.77	45.33
B	100	49.03	41.53

#### 实施例5 催化剂的性能2

采用流化床反应装置, 流化反应器为石英玻璃材质, 用实施例3提供的SAPO-34分子筛催化剂C在600℃条件下用水蒸汽处24小时, 即为定型催化剂E, 将催化剂E 15ml (约10克) 装填在流化反应器内用泵注入甲醇或二甲醚为反应原料。在正式反应试验之前用纯氮在550℃活化处理催化剂E 1小时, 然后切换进甲醇或二甲醚, 进行转化为低碳烯烃的反应, 在反应温度550℃和甲醇重量空速 $6.45 \text{ h}^{-1}$  (或二甲醚重量空速 $7.16 \text{ h}^{-1}$ ) 条件下反应10分钟的结果列于下表3。

表 2

反应原料	烃类产物组成 %wt			
	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> ~C <sub>4</sub>
甲醇	6.33	62.79	22.34	89.57
二甲醚	6.42	59.35	24.22	88.32

### 实施例 6 催化剂的性能 3

采用上述实施例 5 完全相同的流化床反应装置和催化剂 E, 以甲醇为反应原料, 改变反应温度和甲醇进料重量空速, 分别进行 10 分钟, 其结果列于表 4, 在所有反应条件下, 甲醇的转化率均为 100%。

表 4

反应条件		烃类产物组成 %wt			
温度 °C	甲醇重量空速 h <sup>-1</sup>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> ~C <sub>4</sub>
450	5.0	2.0	31.0	38.2	78.4
490	5.0	3.0	35.4	36.3	83.2
530	5.0	4.4	45.6	30.5	87.8
550	5.0	6.3	52.4	23.4	89.0
570	5.0	9.8	60.3	22.1	87.3
550	3.0	6.5	51.2	28.5	88.3
550	6.0	6.2	58.1	23.2	89.5
550	10.0	6.0	62.3	20.0	90.2

比较合适的反应温度范围为  $530 \sim 550^{\circ}\text{C}$ ，以及比较适宜的甲醇重量空速范围  $5.0 \sim 10.0 \text{ h}^{-1}$ 。

#### 实施例7 催化剂再生试验

采用上述实施例5完全相同的流化床反应装置和催化剂E，以二甲醚为原料，对该催化剂E进行反复的反应和催化剂再生试验。再生试验表明在  $550 \sim 650^{\circ}\text{C}$  温度范围内，可直接用空气进行烧焦，所用再生温度低时，烧焦时间长些，反之则可缩短，均可全部烧除焦炭和使催化剂活性恢复。如在  $550^{\circ}\text{C}$  时烧焦，再生可在  $30 \sim 40$  分钟内完成， $650^{\circ}\text{C}$  时则可5分钟之内完成。但适宜再生烧焦条件为  $600^{\circ}\text{C}$ ，10分钟和空气下，其结果列于表5。

表5 连续进行100次再生的试验结果

再生次数	0	10	30	60	80	100
反应温度 $^{\circ}\text{C}$	550	530	530	530	530	530
烯烃选择性 %						
$\text{C}_2$ 选择性 (%)	35.66	49.49	52.55	52.53	52.33	50.69
$\text{C}_3$ 选择性 (%)	39.76	34.09	34.45	31.45	32.08	35.88
$\text{C}_3 \sim \text{C}_4$ 选择性 (%)	87.16	92.19	94.81	92.51	92.66	93.46

反应条件：二甲醚重量空速  $2.0 \text{ h}^{-1}$

二甲醚转化率  $\sim 100\%$ 。